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EXCHANGE OF PHOSPHORUS ISOTOPES IN THE SYSTEMS H_3PO_2 - H_3PO_3 AND KH_2PO_2 - KH_2PO_3 , AND THE TAUTOMERISM OF HYPOPHOSPHOROUS ACID

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The results reported in the paper indicate the absence of isotopic exchange in phosphorus compounds which potentially could be utilized for the enrichment of dispersed radioactive phosphorus by some method other than that involving an isotopic exchange reaction. The results obtained serve as experimental proof of A. Ye. Arbuzov's assumption to the effect that hypophosphorous acid exists in two tautomeric forms.

Research on the isotopic exchange of phosphorus in phosphorus oxyacids and their derivatives has been confined to systems in which one of the components is phosphoric acid (or its anion), with P^{32} (1) as the tracer. In no case has any exchange been discovered, even with prolonged heating (2). This has been explained, as in other similar cases (3), by the coordination stability of the phosphorus atom symmetrically surrounded by four oxygen atoms in the PO_4^{3-} ion. It might be expected that exchange between hypophosphorous and phosphorous acids (or their salts) would be possible, since the bond between the phosphorus atom and the external coordination sphere in them should be weaker.

The study of these systems is particularly interesting as we can assume the existence of the tautomerism of phosphorous acid (4) on the basis of A. Ye. Arbuzov's discovery of the duality of reactions of symmetrical and unsymmetrical derivatives of phosphorous acid and of isomeric conversions of the esters of this acid. Such a tautomerism is highly probable for hypophosphorous acid (4, 5).

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Serving us as the initial radioactive phosphorus compound was Na_2HPO_4 , which was added to barium phosphate $\text{Ba}(\text{H}_2\text{PO}_4)_2$ in solution. The active barium phosphate produced in this manner was dried, mixed with carbon, and calcined to 1,200°. The white phosphorus separating out at this point was collected under water and then boiled with a saturated solution of barium hydroxide. The solution was evaporated on a water bath until crystals of barium hypophosphite appeared, and these were dried at 70°. Free hypophosphorous acid was prepared by the careful interaction of the solution of the barium salt with sulfuric acid, and the acid's potassium salt was obtained by the interaction of the same solution with potassium sulfate. The resultant hypophosphorous acid contained no more than 1% H_3PO_3 , and its potassium salt contained no phosphite.

Ordinary nonradioactive phosphorous acid was obtained by the hydrolysis of phosphorus trichloride and the dessication of the crystals formed. To obtain this acid's calcium salt, the solution was neutralized with alkali.

The total content of both of the phosphorus acids or of their salts in solution was determined by the iodometric method (6). For their separation, we used the differing solubility of the barium salts. Barium phosphite was precipitated with barium nitrate in the presence of acetic acid and sodium acetate (6). The radioactivity of barium phosphite was measured in precipitates of density up to 10 mg/sq cm $\frac{1}{61\text{c}}$. The initial radioactivity of the solutions was measured in the dry residue from the evaporation of a weighed portion by the usual means. The activity of a standard preparation was measured simultaneously with all other measurements.

The activity values cited below are given in counts per minute, corrected against the background (about 30 counts), and calculated for one mole equivalent of phosphorus. Concentrations are given in millimoles per 1 gram of solution.

The exchange experiments yielded the following results: the solution of 0.354-N $\text{KH}_2\text{P}^*\text{O}_2 + 0.522\text{-N } \text{K}_2\text{HPO}_3$ at room temperature (over various time intervals up to 73 hr), yielded precipitates of BaHPO_3 with an activity of 0 ± 10 , while for 100% exchange the activity of these precipitates should have been $870\text{-}750 \pm 20$ in the various experiments. The same result was obtained with heating for 5 hr to 70°, and also in the presence of 2.4-N KOH or 3.3-N HCl after 24 hr at room temperature. The solution of 0.832-N $\text{H}_3\text{P}^*\text{O}_2 + 0.998\text{-N } \text{H}_3\text{PO}_3$ after 8-50 hr at room temperature yielded a precipitate of BaHPO_3 with an activity of 20 ± 10 , instead of $695\text{-}630 \pm 20$, corresponding to 100% exchange. The same result was obtained by heating for 5 hr to 70°, and also upon the addition of 2.0-N HCl in the course of 72 hr at room temperature. In the more accurate experiments, with increased activity of compounds and with weighed portions of the samples being measured, the mixture of 1.035 g of $\text{H}_3\text{P}^*\text{O}_2 + 1.241\text{-N } \text{H}_3\text{PO}_3$ after 208 hr at room temperature and after 6 hr at 70° gave precipitates of BaHPO_3 with an activity of up to 1 ± 3 ; for total exchange the activity of these precipitates should have been equal, respectively, to 590 ± 20 and 900 ± 20 . In the presence of 2.0 N HCl after 6 hr at 70°, the activity was 5 ± 3 .

From the cited data it is evident that between hypophosphorous and phosphorous acids, as well as between their potassium salts, no isotopic exchange of phosphorus takes place, even with heating or in the presence of acids or alkalis.

In certain experiments, iodine was added in a concentration reaching 0.016-0.020-N, which corresponded to a 1.2% oxidation of hypophosphorous acid. This also did not bring about an exchange. The experiments in the presence of iodine were repeated with a higher concentration of it. In one series, with a solution of 0.137-N $\text{H}_3\text{P}^*\text{O}_2 + 0.210\text{-N } \text{H}_3\text{PO}_3$, iodine was added in an amount equal to 0.081-N, which corresponds to a 29.3% oxidation of hypophosphorous acid.

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The following data are presented in Table 1: the quantity of oxidized acid found by iodometric titration; the observed number of counts produced by the BaHPO_3 precipitate; and the number of counts corresponding by calculation to the quantity of radioactive iodine [sic; should be phosphorus], which passed into the phosphorous acid as a result of the oxidation of hypophosphorous acid. Both values agree to within 3%, which corresponds to errors in measurement. The difference between them does not increase with time. All this points to the absence of exchange between both acids. A complete exchange would yield the number of counts shown in the last column of Table 1.

Table I. Exchange Data for 29.3% Oxidation of Hypophosphorous Acid

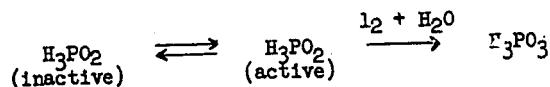
Time (hr)	Temp (°C)	% Oxidation	Observed	No of Counts/Min	
				Calculated From % Oxidation	Calculated for 100% Exchange
1	Room	28.9	2,340	2,180	5,100
6	"	30.4	2,410	2,240	5,050
93	"	28.9	1,620	1,620	4,240
117	"	30.3	1,470	1,470	4,040
7	70	31.8	2,310	2,160	4,650
			± 40	± 50	

Nor is exchange brought about by the addition of potassium iodide in 0.377-N concentration to a solution of 0.649-N $\text{H}_3\text{F}^*\text{O}_2$ + 0.995-N H_3PO_3 , which corresponds to a 19% reduction of phosphorous acid.

The absence of exchange in the presence of iodine or its anion requires a special explanation. In the oxidation-reduction system $\text{H}_3\text{PO}_2 + \text{I}_2 + \text{H}_2\text{O} = \text{H}_3\text{PO}_3 + 2\text{I}^- + 2\text{H}^+$ there certainly are forward and reverse reactions which should lead to exchange with a velocity commensurate with the velocity of the reactions of oxidation or reduction. In the analogous $\text{H}_3\text{As}^*\text{O}_2 - \text{H}_3\text{AsO}_3$ system in the presence of iodine or in $\text{I}_2^* + \text{IO}_3^-$ (7), exchange proceeds easily.

The absence of exchange in the systems which we investigated would be most easily explained by the irreversibility of the reactions of oxidation of hypophosphorous acid and reduction of phosphorous acid. However, on the basis of chemical data, there is no doubt that these reactions are reversible.

The contradiction is eliminated if we assume the existence of two tautomeric forms of hypophosphorous acid: the ordinary "inactive," asymmetrical $\text{O} = \text{P}^{\text{V}}\text{H}_2(\text{OH})$ and the "active," symmetrical $\text{HPH}_2(\text{OH})_2$. The conversion of the first into the second precedes the oxidation by iodine. This conversion is a slow stage which determines the kinetics of the whole reaction, while the stage of interaction with iodine takes place rapidly and practically irreversibly:



The reaction reducing the phosphorous acid must take place by the same stages in the opposite direction. The first reversible reaction cannot lead to exchange. The second would produce an exchange if it proceeded reversibly, but, since it proceeds irreversibly, there is no exchange.

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The kinetic investigations of a group of authors (5) have led to the same oxidation reaction scheme. The data obtained in this work can be considered as a substantial confirmation of the widespread, but until now not directly substantiated, hypothesis on the tautomerism of hypophosphorous acid, because it would be difficult to explain the matter otherwise.

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